



# **Technical Language Service**

Translations From And Into Any Language

## **JAPANESE / ENGLISH TRANSLATION OF**

**Japanese Patent Application JP 7 – 291896 A**

**Title: Method for Manufacturing High-Purity Terephthalic Acid**

**Your Ref: No. 9144**

**For: Eastman Chemical Company -  
Library and Information Services (LibriS)**

(19) Japanese Patent Office (JP) **(12) Unexamined Patent Gazette (A)** <sup>(11)</sup> Unexamined Patent Application No:  
**Kokai 7-291896**

(43) Date of Publication: November 7, 1995

(51) Int. Cl. <sup>6</sup>	Class. Symbols	Internal Office Registration Nos.:	FI	Technical Classification Field
C 07 C 63/26	J	9450-4H		
B 01 J 31/26	X			
C 07 C 51/265				
51/43				
51/487				

Request for Examination: Not yet submitted

Number of Claims: 1 OL

(Total of 7 pages [in original])

(21) Application No.: 6-88342  
(22) Date of Filing: April 26, 1994

(71) Applicant: 000004466  
Mitsubishi Gas Chemical Company, Inc.  
2-5-2 Marunouchi  
Chiyoda-ku, Tokyo  
(71) Applicant: 000003160  
Toyobo Co., Ltd.  
2-2-8 Dojimahama, Kita-ku  
Osaka-shi, Osaka-fu  
(71) Applicant: 592162324  
Mizushima Aroma Co., Ltd.  
2-3-1 Mizushima Nakadori  
Kurashiki-shi, Okayama-ken  
(72) Inventor: Fumiya Arima  
c/o Mitsubishi Gas Chemical Company, Inc.  
3-10 Mizushima Kaigandori  
Kurashiki-shi, Okayama-ken

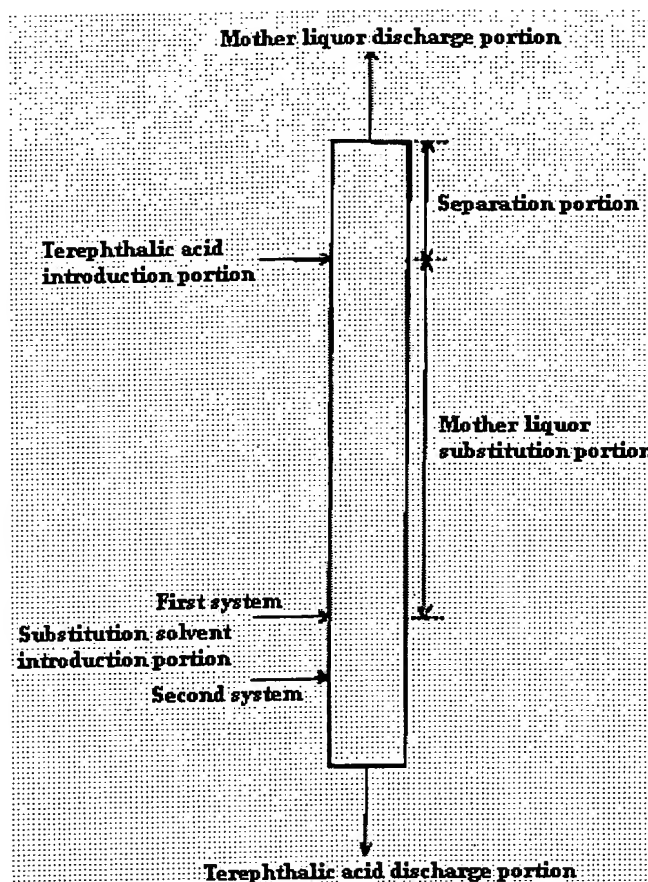
(54) [Title of the Invention]

**Method for Manufacturing High-Purity  
Terephthalic Acid**

**(57) [Summary]**

**[Object]** To provide a method for manufacturing high-purity terephthalic acid with less energy and at a lower cost.

**[Constitution of the Invention]** When treating terephthalic acid after the crude terephthalic acid solution has been refined, a substitution solvent that flows as a rising stream within the mother liquor substitution column, and a substitution solvent for discharging the terephthalic acid from the bottom of the mother liquor substitution column are respectively kept at their required temperatures, and are introduced to mother liquor substitution column by means of two systems.



**[Claims]**

**[Claim 1]** A method for manufacturing high-purity terephthalic acid, characterized in that liquid-phase oxidation of a *p*-phenylene compound having a carboxyl group and/or a carboxyl group-generating oxidizable substituent group in the para positions is carried out in the presence of a transition metal compound; the resulting crude terephthalic acid is refined by oxidation, reduction, or other reactions, or by recrystallization; the terephthalic acid crystal slurry solution wherein the pressure and temperature are reduced to adjust the temperature thereof to between 120 and 220°C is thereafter introduced to the top of the mother liquor column; the substitution solvent of the first system is fed from the bottom of the mother liquor substitution column at a temperature that is equal to or within 100°C of the temperature of the introduced terephthalic acid crystal slurry; the substitution solvent of the second system is fed from the bottom at a temperature that is 5 to 120°C lower than the temperature of the substitution solvent of the first system, and terephthalic acid crystals are precipitated; the mother liquor of the terephthalic acid crystal slurry solution mainly introduced from the column top and the substitution solvent of the

first system are discharged; the terephthalic acid crystals precipitated in the column mainly from the mother liquor substitution column bottom, and the slurry solution of the second system are discharged; and the terephthalic acid crystals are separated from the slurry solution that was discharged from the column bottom.

### **[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]** The present invention relates to a method for manufacturing high-purity terephthalic acid, which is a principal crude material for the polyester resins widely used in fibers, film, industrial materials, common molded products, and other products.

**[0002]**

**[Prior Art]** Terephthalic acid is ordinarily manufactured using acetic acid as a solvent under high temperature and high pressure by the air oxidation of *p*-xylene in which an accelerator such as a bromine compound as a cocatalyst or acetic aldehyde has been added to a cobalt or manganese catalyst. However, crude terephthalic acid resulting from this liquid-phase air oxidation normally has inferior whiteness; large quantities of 4-carboxybenzaldehyde (4CBA), *p*-toluic acid (pTOL), or other impurities are contained therein; and this crude terephthalic acid is not directly suitable for reaction with glycol to form polyester. Methods for manufacturing terephthalic acid have also been proposed whereby acetic is used as a solvent in the same manner as described above, and liquid-phase oxygen oxidation is carried out under high pressure and temperature using a cobalt catalyst. However, the by-production of 4CBA and other impurities is considerable in these methods as well, and, in the same manner as the above-described method, this crude terephthalic acid cannot be directly used in reactions with glycol or the like.

**[0003]** Methods (catalytic hydrogenation, catalytic treatment, recrystallization, oxidation, reslurrying, a combination of these, or another method carried out in the presence of a Group VIII noble metal catalyst at high temperature) in which the refining treatment is carried out by oxidation, reduction, or another reaction, or simply by recrystallization are known as methods for manufacturing high-purity terephthalic acid from crude terephthalic acid containing 4CBA and other such impurities, but mainly catalytic hydrogenation is currently carried out on

commercial scale. For example, a method for catalytically hydrogenating an aqueous solution of crude terephthalic acid in the presence of a Group VIII noble metal catalyst in a high-temperature solvent of 230°C or higher is disclosed in JP (Kokoku) 41-16860, and an improvement method thereof is also disclosed in JP (Kokoku) 47-49049.

[0004]

**[Problems to Be Solved by the Invention]** Proposed in JP (Kokoku) 47-49049 is a process in which the cooling velocity by water evaporation is kept at 2.2 to 5.5°C per minute, and crystal separation is carried out in a temperature range of 120 to 150°C in order to prevent pTOL contamination when crystallizing terephthalic acid from a hydrogenated crude terephthalic acid solution. JP (Kokoku) 47-49049 describes a batch-type crystallization method, and in accordance with an experiment performed by the present inventor, the difficulty of controlling the cooling velocity in the continuous crystallization tanks was confirmed when crystallizing terephthalic acid crystals with a continuous crystallization process whereby the solution passes through a plurality of crystallization tanks disposed in a straight line in a manner that simulates an apparatus adapted for manufacturing the product on a commercial scale.

[0005] In other words, the method of JP (Kokoku) 47-49049 is a method in which the temperature of the slurry solution is reduced through water evaporation by setting the pressure in each stage of the crystallizer to a pressure that is lower than each previous stage of the crystallizer. However, the temperature reduction is essentially performed instantaneously in each crystallizer until a temperature that corresponds to the set pressure is achieved downstream from the metering valve located between the current crystallizer and the previous-stage crystallizer. Therefore, to actually implement the cooling velocity stipulated in JP (Kokoku) 47-49049 with a continuous crystallization method, a crystallization tank with twenty stages or more is required, and is not practical from the aspect of industrial production.

[0006] The cooling velocity can be relatively freely controlled in batch-type crystallization, but the present inventor, as a result of actual experimentation with the batch-type crystallization method, found that the cooling velocity of 2.5 to 5.5°C was not particularly relevant, and that carrying out crystal separation in a temperature range of 120 to 150°C was effective in preventing pTOL contamination in the terephthalic acid crystals. The centrifugal separation,

filtering, and other methods are proposed in JP (Kokoku) 47-49049 as methods for separating crystals from a crystal slurry at a high temperature and pressure.

[0007] Centrifugal separation entails introducing a slurry solution to a cylindrical or columnar casing rotating at a high speed, causing the mother liquor to overflow from the top portion, and scraping the lower portion with blade so that crystals adhering to the casing wall are discharged. However, washing the crystals is difficult in centrifugal separation, large quantities of impurities are dissolved in the mother liquor adhering to the crystals, and even when this is dried, high-purity terephthalic acid cannot be obtained. For this reason, the separated terephthalic acid cake must be reslurried with high-temperature water, and the separation step must be repeated. Daily maintenance and management of the apparatus is laborious because of the need to carry out centrifugal separation at a high temperature and pressure with a high-speed rotation and because of the need to make higher capital investment for auxiliary equipment.

[0008] An improvement method for performing filtration at high temperature and high pressure has been proposed to overcome the drawbacks of centrifugal separation. The use of a rotary vacuum filter at high temperature and pressure is cited in JP (Kokai) 1-299618, for example, but this type of filtration at high temperature and pressure is difficult to implement on a large scale. Also proposed are several methods that apply a liquid cyclone separator, but all of these have an inadequate substitution ratio for the mother liquor.

[0009]

**[Means Used to Solve the Above-Mentioned Problems]** The present inventor has proposed and filed a patent application (Japanese Patent Application 05-299465) for a mother liquor substitution method as a solution to the above-described drawbacks when crystallizing high-purity terephthalic acid from a catalytically hydrogenated crude terephthalic acid solution. This method uses a mother liquor substitution column, and substitutes the mother liquor of the terephthalic acid crystal slurry solution with a fresh solvent, allowing high-purity terephthalic acid to be easily obtained. However, in this mother liquor substitution method, a separate heat source for water vapor is required in order to heat the entire amount of substitution solvent to the treatment temperature of the terephthalic acid crystal slurry solution. The present inventor, as a result of further investigation concerning such a mother liquor substitution method, arrived at the present invention having discovered that a low-temperature heat source used in the process can

be effectively used, lower energy use can be ensured, and lower costs for high-purity terephthalic acid can be achieved by dividing the substitution solvent into two systems and setting the temperature separately for each system.

[0010] In other words, the present invention is a method for manufacturing high-purity terephthalic acid characterized in that liquid-phase oxidation of a *p*-phenylene compound having a carboxyl group and/or a carboxyl group-generating oxidizable substituent group in the para positions is carried out in the presence of a transition metal compound; the resulting crude terephthalic acid is refined by oxidation, reduction, or other reactions, or by recrystallization; the terephthalic acid crystal slurry solution wherein the pressure and temperature are reduced to adjust the temperature thereof to between 120 and 220°C is thereafter introduced to the top of the mother liquor column; the substitution solvent of the first system is fed from the bottom of the mother liquor substitution column at a temperature that is equal to or within 100°C of the temperature of the introduced terephthalic acid crystal slurry; the substitution solvent of the second system is fed from the bottom at a temperature that is 5 to 120°C lower than the temperature of the substitution solvent of the first system, and terephthalic acid crystals are precipitated; the mother liquor of the terephthalic acid crystal slurry solution mainly introduced from the column top and the substitution solvent of the first system are discharged; the terephthalic acid crystals precipitated in the column mainly from the mother liquor substitution column bottom, and the slurry solution of the second system are discharged; and the terephthalic acid crystals are separated from the slurry solution that was discharged from the column bottom.

[0011] The crude terephthalic acid used for manufacturing the high-purity terephthalic acid of the present invention is obtained by the liquid-phase oxidation of a *p*-phenylene compound. The *p*-phenylene compound that is used is one having a carboxyl group and/or an oxidizable substituent group that generates a carboxyl group as a result of liquid-phase air oxidation in the para positions. Examples of the substituent group include the methyl group, ethyl group, propyl group, isopropyl group, formyl group, and acetyl group. These substituent groups may be mutually the same or different. The *p*-phenylene compound used for manufacturing crude terephthalic acid is most commonly *p*-xylene.

[0012] Water or acetic acid, or a mixture of these may be used as the solvent for the liquid-phase oxidation. Manganese, cobalt, iron, chrome, nickel, or other transition metal compounds may be used as a catalyst in liquid-phase oxidation; a bromine compound is normally used as the

cocatalyst, but when a bromine compound is not used, acetic aldehyde and methyl ethyl ketone are used in combination as an accelerator when a cobalt catalyst is used. The catalyst that is used is not particularly limited as long as cobalt ions, manganese ions, iron ions, chrome ions, nickel ions, or bromine ions are generated in the oxidation reactor. Oxygen or air is used as the oxidizing agent in liquid-phase oxidation. Air is adequate for oxidation in the presence of a cobalt or manganese catalyst, or bromine compound in an acetic acid solution, and oxygen is preferably used in oxidation in the presence of a cobalt catalyst in an acetic acid solution.

[0013] The crude terephthalic acid resulting from liquid-phase oxidation in an acetic acid solution ordinarily contains a considerable amount of impurities such as 4CBA, and the OD340 value (which is a hue index) is also not at a level that allows the product to be directly used as a polymer crude material for molding, so a refining step is normally required. The OD340 value and the quantity of 4CBA or other impurities in the crude terephthalic acid are not particularly limited in the refinement treatment. The present invention is one in which crude terephthalic acid is refined by oxidation, reduction, or other reactions, or by recrystallization, and the terephthalic acid crystal slurry solution is thereafter subjected to solvent substitution. As cited in prior art, examples of some of the several refinement methods include catalytic hydrogenation, catalytic treatment, recrystallization, oxidation, and reslurrying. The terephthalic acid refined by any of these methods may be used in the solvent substitution of the present invention, but catalytic hydrogenation is most commonly used, so following is a description of hydrogenation.

[0014] The catalytic hydrogenation is carried out at a high temperature and pressure in a solution state, and the temperature of the catalytic hydrogenation is 230°C or higher, and preferably is in a temperature range of 240 to 300°C, in the presence of hydrogen. The concentration of the crude terephthalic acid is preferably in a range of 10 to 40 wt%, so it is preferable to establish a pressure that is adequate for maintaining a liquid phase and ensuring a partial hydrogen pressure suitable for a catalytic hydrogenation reaction, normally in a range of 30 to 80 atm. A Group VIII noble metal is used as the catalyst for the catalytic hydrogenation reaction, and the Group VIII noble metal is preferably palladium, platinum, ruthenium, or rhodium, but particularly preferred is palladium. The catalytic hydrogenation catalyst is ordinarily supported on a carrier. A porous substance is normally used as the carrier, but materially preferred is a carbon-based carrier, and activated carbon, and particularly coconut charcoal, is advantageous. Even a small amount of catalyst supported by the carrier is effective, and the range is not



particularly limited, but a supported amount of about 0.1 to 1.0 wt% is advantageous for maintaining long-term activity.

[0015] Water or acetic acid, or a combination of these may be used as the catalytic hydrogenation solvent. The amount of hydrogen that must be supplied for catalytic hydrogenation is at least two or more molar amounts with respect to 4CBA. The catalytic hydrogenation should last for a time that is sufficient to essentially allow the hydrogenation reaction to progress, and is ordinarily in a range of 1 to 60 minutes, and preferably 2 to 20 minutes. Catalytic hydrogenation is normally performed with the continuous method. The crude terephthalic acid solution subjected to catalytic hydrogenation prevents contamination from fine powder, which is caused, for example, by abrasion of the activated carbon used as the catalytic carrier, so the solution is filtered with a filter composed of a corrosion-resistant material, thereafter introduced to a batch-type crystallizer or a crystallizer with two to six stages linked in series, and cooled to a temperature of 120 to 220°C by solvent evaporation in which the pressure in the crystallizer is sequentially reduced to crystallize the terephthalic acid crystals and form a slurry solution. The slurry solution obtained in this manner is composed of mother liquor that contains large quantities of terephthalic acid crystals and impurities, and the mother liquor containing a considerable quantity of impurities is substituted with a fresh substitution solvent to obtain high-purity terephthalic acid by the mother liquor substitution of the present invention.

[0016] Following is a description of the mother liquor substitution tower with reference to the diagram. Fig. 1 is a schematic view of the mother liquor substitution column used in the method of the present invention. The mother liquor substitution column, as shown in Fig. 1, is a column-type apparatus, and has an introduction portion for terephthalic acid slurry moved from the previous step at the column top, a substitution solvent introduction portion for the second system in the lower portion of the column, a discharge portion for mother liquor that contains impurities at the top portion of the column, and a discharge portion for terephthalic acid subjected to solvent substitution in the lower portion of the column. The functions of the mother liquor substitution column include a crystal classifying effect between the column top and the substitution solvent introduction portion, a crystal precipitation/washing and mother liquor substitution effect between the slurry introduction portion and the substitution solvent introduction portion, and an effect for slurring the terephthalic acid crystals and the substitution solvent between the substitution solvent introduction portion and the terephthalic acid discharge

portion. The mother liquor substitution column may be one devoid of internal structural components, but a column with a so-called RDC (Rotary Disk Contactor) structure, a column with a tier structure, a column divided into long passages, or another mother liquor substitution column with an internal structure may also be used.

[0017] The substitution solvent used in the present invention may be water or acetic acid in accordance with the solvent used in catalytic hydrogenation, or a mixture of these may be used. The substitution solvent is divided into two systems and introduced from the lower portion of the mother liquor column in the present invention. The substitution solvent of the first system flows mainly as a rising stream in the mother liquor substitution column, makes countercurrent contact with the terephthalic acid crystals that precipitate from the upper portion of the mother liquor substitution column, subsequently mixes with the crude slurry fed to the mother liquor substitution column, and passes through the classifying portion to be discharged from the top of the column. The substitution solvent of the second system fed to the lower portion mixes with the terephthalic acid crystals that precipitate from the mother liquor substitution portion. This forms a slurry composed of high-purity terephthalic acid and the substitution solvent that is discharged from the bottom of the column.

[0018] The temperature of the substitution solvent of the first system, which is the rising stream in the mother liquor substitution column, is essentially set to the same temperature as the terephthalic acid crystal slurry solution introduced to the upper portion of the mother liquor substitution column, but the temperature may be set to yet a lower temperature, and the cost required to heat the substitution catalyst can be reduced by setting the temperature of this substitution solvent to be low. However, increasing the temperature difference between the substitution solvent that flows as a rising stream in the mother liquor substitution column and the terephthalic acid crystal slurry solution introduced to the upper portion of the mother liquor substitution column is limited as such, and various problems tend to arise in overcoming this limitation. In other words, when the temperature difference increases, the terephthalic acid precipitates and adheres to the surface of the walls of the mother liquor substitution column, plugging tends to occur, pTOL and other impurities precipitate together with the precipitation of terephthalic acid, and the quality of the terephthalic acid degrades. The precipitation velocity of the terephthalic acid crystals decreases, so the column diameter of the mother liquor substitution column must be increased. This not only leads to an increase in capital spending, but also makes

it difficult to control the rising liquid stream of substitution solvent in an orderly manner, and compromises the effect of improved quality. Therefore, the temperature of the substitution solvent of the first system that flows as a rising stream in the mother liquor substitution column should be at a level that is equal to or within 100°C of the temperature of the terephthalic acid crystal slurry solution to be introduced to the upper portion of the mother liquor substitution column. The linear velocity of the rising stream of substitution solvent varies in accordance with the structure of the device, the crystal size, and other factors, but is preferably about 0.1 to 3.0 m/hr. If the linear velocity is excessively low, the separation of the terephthalic acid crystals from the mother liquor is inadequate, and the purity of the terephthalic acid discharged from the lower portion of the column is reduced. If the linear velocity is conversely excessively high, more substitution solvent is used.

[0019] The substitution solvent of the second system discharged from the bottom of the mother liquor substitution column together with the terephthalic acid crystals, which were introduced to the lower portion via the first system in the mother liquor substitution column and precipitated within the mother liquor substitution column, is such that the mother liquor has already been substituted in the lower portion of the mother liquor substitution column and pTOL and other impurities are minimal, so the precipitation of impurities has little effect on the quality of the terephthalic acid. Therefore, the temperature of the substitution solvent of the second system discharged as a slurry together with terephthalic acid, which was introduced to the lower portion of the mother liquor substitution column, from the bottom of the mother liquor substitution column is set lower than the substitution solvent of the first system, is a temperature that is 5 to 120°C lower than the temperature of the substitution solvent of the first system, and is preferably in a temperature range that is lower than the boiling point of the substitution solvent at normal pressure, but higher than 60°C.

[0020] The substitution solvent of the second system in the present invention is mainly discharged from the bottom of the mother liquor substitution column. When the concentration of the slurry composed of the substitution solvent and terephthalic acid crystals discharged from the bottom of the mother liquor substitution column is excessively high, the slurry becomes difficult to handle; and when the slurry concentration is low the treatment load for the mother liquor to be separated from the crystallization tank increases, so the slurry concentration is preferably about the same concentration as the terephthalic acid crystal slurry introduced to the mother liquor

substitution column. Thus, when the concentration of the slurry discharged from the bottom of the mother liquor substitution column is about the same as the slurry introduced to the mother liquor substitution column, the amount of substitution solvent in the second system is substantially the same as the amount of mother liquor in the terephthalic acid crystal slurry introduced to the mother liquor substitution column.

[0021] The mother liquor discharged from the column top contains, in slurry form, terephthalic acid in an amount that corresponds to the solubility at the temperature of the liquor, and fine terephthalic acid crystals discharged in conjunction with the rising stream in the classified portion. This mother liquor passes through one to three crystallization tanks disposed in series, so the liquid flow is cooled to the minimal possible temperature to form terephthalic acid crystals. The terephthalic acid is separated and recovered from the mother liquor with a filter or another suitable device. Terephthalic acid is contained in an amount that corresponds to the solubility at that temperature together with other organic components in the mother liquor discharged by the separation and recovery operation, so the mother liquor may be passed through a further recovery step or sent directly to a waste treatment step.

[0022] The liquid flow discharged from the top of the mother liquor substitution column is a slurry solution of the substitution solvent containing refined terephthalic acid crystals. This liquid flow passes through one to three crystallization tanks disposed in series, so the liquid flow is cooled to 50 to 110°C. The terephthalic acid crystals are separated in the crystal separator, discharged, and dried via a drying step, yielding high-purity terephthalic acid crystals. The mother liquor discharged from the crystal separator at this point contains only terephthalic acid corresponding to the solubility at that temperature, and other organic and inorganic impurities are at a very low concentration, so the mother liquor is effectively reused as a solvent for dissolving crude terephthalic acid for catalytic hydrogenation.

[0023] The amount of the substitution solvent of the first system is determined by the linear velocity of the rising stream inside the column, as described above, but the amount of the substitution solvent of the first system is equal to or less than half of the slurry introduced to the mother liquor substitution column to carry out efficient operation of the mother liquor substitution column. However, the amount of substitution solvent of the second system is substantially the same as the amount of mother liquor in the terephthalic acid crystal slurry introduced to the mother liquor substitution column, so the amount of substitution solvent of the

second system accounts for most of the substitution solvent introduced to the mother liquor substitution column, and the cost of heating the substitution solvent can be considerably reduced by setting this temperature low. In the method of the present invention, the amount of substitution solvent of the second system is considerable, and the temperature thereof can be set low, so low-pressure steam generated by a low-pressure crystallization tank, for example, or another low-temperature heat source used in the process can be effectively used to heat the substitution solvent, and the cost of energy used in the terephthalic acid manufacturing apparatus can be significantly reduced. The cooling load is reduced by effectively using a low temperature heat source in the process, and the cooling load for treating the slurry solution discharged from the bottom of the mother liquor substitution column is also reduced. In some cases, the number of crystallization tanks can be reduced, so a lower cost high-purity terephthalic acid can be ensured.

**[0024]**

**[Working Examples]** The present invention is more specifically described below with working examples. However, the working examples do not impose any limitation on the present invention.

**[0025] (Working Example 1)**

Crude terephthalic acid was manufactured using a commercial-scale apparatus. In other words, manganese acetate, cobalt acetate, and hydrogen bromide were used as catalysts; and *p*-xylene was oxidized with air in a hydrated acetic acid solvent at a temperature of 205°C and a pressure of 17 atm. Next, 200 mL of a catalyst in which 0.5% palladium was supported on activated carbon was loaded into a hydrogenation reactor that was equipped with an external heating device and had a length of 350 mm and an inside diameter of 26 mm. The hydrogenation reactor had a receptacle and a cooler for cooling the hydrogenation fluid to a predetermined temperature, and the receptacle was connected to the mother liquor substitution column. The mother liquor substitution column was one devoid of internal structural components, and was equipped with an external jacket with an inside diameter of 28 mm and a height of 2,500 mm. The slurry solution introduction port was disposed in a position 2,300 mm from the bottom surface of the column, the substitution water introduction port of the first system was disposed in a position 200 mm from the bottom surface of the column, and the substitution

water introduction port of the second system was disposed in a position 100 mm from the bottom surface of the column. Receptacles with a capacity of 200 L were connected to the respective discharge ports at the top and bottom of the column, and a heating device, reflux condenser, and agitating device were mounted on the receptacle.

[0026] The hydrogenation reactor was heated to 285°C, and a 25% aqueous solution of the above-described crude terephthalic acid heated to 285°C was fed at a rate of 1,400 g per hour as hydrogen gas was fed from a hydrogen gas supply line to the terephthalic acid aqueous solution at a rate of 0.4 NL per hour to carry out catalytic hydrogenation. The hydrogenation liquid that flowed from the reactor was cooled to 150°C and held in a receptacle. In advance of operation of the mother liquor substitution column, substitution water heated to a temperature of 150°C was introduced through the substitution water introduction port of the first system at a rate of 470 g per hour, the mother liquor substitution column was filled with the substitution water, and the material was discharged from the discharge port at the top of the column to a receptacle.

Next, the substitution water heated to a temperature of 100°C was introduced through the substitution water introduction port of the second system at a rate of 2120 g per hour, and discharged from the discharge port at the bottom of the column to a receptacle. After the above operations were completed, terephthalic acid crystal slurry solution heated to 150°C and passed through the above-described catalytic hydrogenation step was introduced from the slurry solution introduction port at the top of the mother liquor substitution column at a rate of 2,860 g per hour, and discharged from the bottom of the mother liquor substitution column at a rate of 2,900 g per hour. The slurry solution containing fine crystals was discharged from the column top at a rate of 2,550 g per hour. The terephthalic acid crystal slurry discharged from the column bottom was cooled to 90°C. The slurry solution was held for about 15 minutes, and rapidly filtered thereafter with an adequately heated G3 glass filter. The crystals were then washed with hot water and dried.

[0027] As a result, the slurry solution with a terephthalic acid concentration of 28 wt% introduced to the mother liquor substitution column was discharged from the bottom of the mother liquor substitution column as a slurry in which the terephthalic acid concentration was 27 wt%. Terephthalic acid (total amount in a solution state and as fine crystals) was discharged from the column top at a rate of 18 g per hour. This corresponds to 2.2 wt% of the terephthalic acid introduced to the mother liquor substitution column in terms of terephthalic acid. The

analyzed values of the resulting terephthalic acid crystals obtained from the crude terephthalic acid are as noted in Table 1.

[0028] (Comparative Example 1) The temperature of the substitution water introduced to the substitution water introduction port of the second system of the mother liquor substitution column was set to 150°C, and the introduction rate of substitution water was 2,120 g per hour. Other conditions were kept the same as the working example. As a result, the slurry solution with a terephthalic acid concentration of 28 wt% introduced to the mother liquor substitution column was discharged from the bottom of the mother liquor substitution column as a slurry in which the terephthalic acid concentration was 27 wt%. The analyzed values of the terephthalic acid crystals are as noted in Table 1.

[0029]

[Table 1]

	Raw material crude TA	Working example	Comparative example
Temperature of mother liquor substitution column (°C)	-	150	150
Temperature of substitution water (first system) (°C)	-	150	150
Temperature of substitution water (second system) (°C)	-	100	150
Refined terephthalic acid analyzed values			
pTOL (ppm)	92	104	101
OD340	1.50	0.082	0.080
4CBA (ppm)	2930	6	6

(Key symbols)

TA: Terephthalic acid

pTOL: *p*-toluic acid

4CBA: 4-carboxybenzaldehyde

[0030] It is apparent from a comparison of the working and comparative examples in Table 1 that there is substantially no difference in the quality of the refined terephthalic acid, and that the cost required for heating the substitution water in the working example is considerably less than in the comparative example because most of the substitution water in the working example was introduced to the mother liquor column at a temperature of 100°C.

[0031]

[Effect of the Invention] When treating a slurry solution in a mother liquor substitution column after crude terephthalic acid solution has been refined, a substitution solvent that flows as a rising

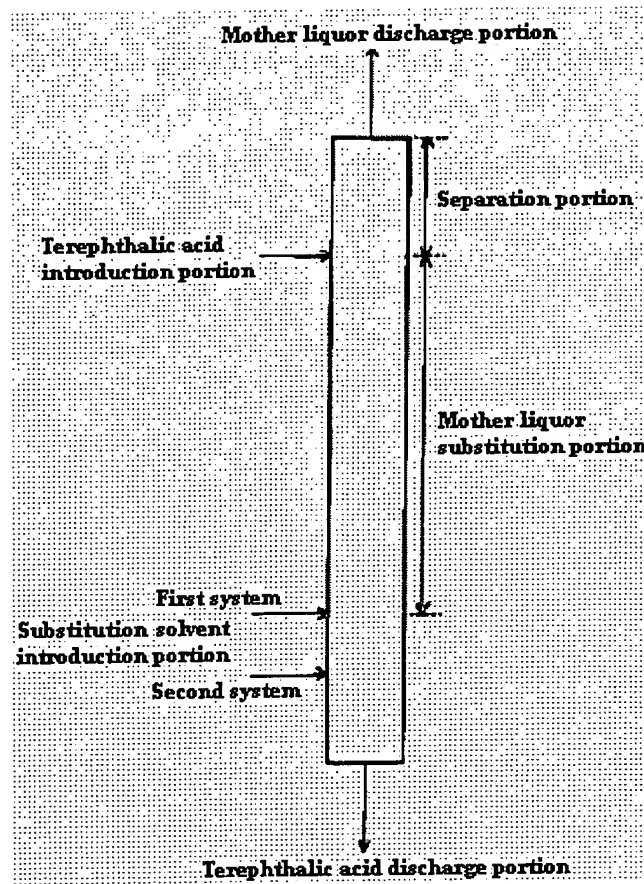
stream within the mother liquor substitution column, and a substitution solvent for discharging the terephthalic acid from the bottom of the mother liquor substitution column are respectively kept at their required temperatures and are introduced to mother liquor substitution column by means of two systems, so the cost of heating the substitution solvent can be considerably reduced while maintaining the quality of the high-purity terephthalic acid. In other words, the amount of substitution solvent used of the second system for discharging terephthalic acid from the top of the mother liquor substitution column is considerable, and this solvent is fed at a low temperature, so the cooling load and the amount energy used can be significantly reduced. The cooling load for treating the slurry solution discharged from the bottom of the mother liquor substitution column can be reduced, and, in some cases, the number of crystallization tanks can be reduced, so a lower-cost high-purity terephthalic acid can be produced.

**[Brief Description of the Drawings]**

**[Figure 1]** A schematic view showing the structure of the mother liquor substitution column used in the method of the present invention.



Fig. 1



(Continued from front page)

(51) Int. Cl.<sup>6</sup>  
// C 07 B 61/00

Class. Symbols  
300

Internal Office  
Registration Nos.:

FI

Technical Classification  
Field